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**Trace metal fractionation as a mean to improve on the management of
contaminated sediments from runoff water infiltration basins**

Amelène El-Mufleh^a, Béatrice Béchet^a, Anne Gaudin^b, Véronique Ruban^a

^a *PRES LUNAM, French Institute of Science and Technology for Transport, Development and Networks (IFSTTAR), Department of Geotechnics, Water and Risks, Centre de Nantes, Route de Bouaye CS4, Bouguenais, F 44344, France*

e-mail: amelene.el-mufleh@ifsttar.fr, beatrice.bechet@ifsttar.fr, veronique.ruban@ifsttar.fr

^b *Laboratoire de Planétologie et de Géodynamique, UMR 6112, Université de Nantes, CNRS, Nantes Atlantique Universités, Nantes, France*

e-mail : anne.gaudin@univ-nantes.fr

Corresponding author:

Béatrice BECHET

Beatrice.bechet@ifsttar.fr

Phone : +33 (0)2 40 84 56 87

Fax : + 33 (0)2 40 84 59 98

Trace metal fractionation as a mean to improve on the management of contaminated sediments from runoff water infiltration basins

The management of stormwater sediment is a key issue for local authorities due to their pollution load and important tonnages. In view of reuse, e.g. for embankment, the environmental evaluation of these highly aggregated sediments requires studying trace metals fractionation and mobility. The distribution of trace metals (Cd, Cr, Cu, Ni, Pb, Zn) and their level of lability in three French stormwater sediments was determined using sequential and kinetic extractions (EDTA reagent) associated with mineralogical analysis and SEM observations. Using microanalysis, new data were acquired on the evolution of aggregate state during extractions and on its significant role in trace metals retention. Trace metals were, in particular, observed to be very stable in small aggregates (10-50 μm). The comparison of the two extraction methods pointed out that EDTA extraction was not convenient to evaluate the stable fraction of Cr, Ni and Zn. Moreover, the results were relevant for basins presenting similar trace metals sources, whatever the physicochemical conditions in basins. The results suggest that the management of stormwater sediments could be improve by a better knowledge of metal mobility, as far as chemical extractions could highlight the localisation of the mobile trace metals fraction. Treatment could be therefore avoided or specific treatment could be applied to a reduced volume of sediments.

Keywords: Urban stormwater sediment, Retention/infiltration basins, Trace metal fractionation, Microanalysis, Sediment management

1. Introduction

Retention and infiltration basins are widely used in urban stormwater management to provide protection from flooding, recharge of aquifers and improvement of downstream waters quality. Runoff waters collected in these basins may actually carry significant loads of pollutants, present as soluble or particulate substances [1-3]. These basins are supposed to accumulate large quantities of sediment over time by decantation and trap pollutants such as trace metals, nutrients and PAHs [4;5]. After few years, clogging is frequently observed, modifying the infiltration ability account would appear necessary in order to maintain both the hydraulic and depuration performance of these ponds. But the removal and disposal of residue represent a key issue for local authorities as far as estimates and surveys show that tonnages are important and represent each year in France, several million tons of dry matter and in an agglomeration scale, tens of thousands of tons [6]. Due to their low organic matter content, their spreading on agricultural land is not recommended and landfill deposit or incineration is very costly. Treatment and/or reuse (e.g. for embankment) seem to be a right compromise. Thus the underlying question is about the sediments quality towards the impact on close environment, in particular towards the migration of pollutants. Consequently, a strong knowledge of the inherent characteristics of the materials is required. Among these characteristics, the mobility of associated pollutants to solid phases is strongly related to their speciation, defined as the distribution of an element amongst different chemical species in a system [7]. However, a direct determination of the speciation of an element is often not attainable, but in many cases, fractionation can provide useful information on release availability. Fractionation is defined as a process of classification of an analyte or group of analytes from a sample according to physical or chemical properties [7;8]. Furthermore, the knowledge of the pollutants mobility within solid phases, could avoid treating the whole sediment. As no legislation for stormwater sediment management was produced until now, in

particular standardized tests to verify the safety of these sediments, it could be convenient to use well known, referenced and fairly simple to implement methods to assess pollutants mobility and improve the treatment of the sediments.

Regarding metallic pollutants, sequential and kinetic extractions are the most widely used fractionation methods to assess the “operationally defined” distribution of metallic pollutants in the different solid phases of a material and to evaluate the potential mobility of these metals, respectively. A few studies using sequential extraction methods were carried out on basin sediments to study trace metal fractionation [9]. However, to our knowledge kinetic extractions were never carried out on basin sediments.

The objective of this study was to examine trace metals fractionation, in order to access to their potential mobility within physical phases. The methodology used is based on the comparison of sequential and kinetic extractions in order to define the fractionation of trace metals on the different solid phases of the sediments [10;11]. To support the results of extractions, mineralogical analysis (XRD) and microscopic observations (SEM-EDX) were performed to assess the nature of mineral phases of the sediments and to ensure the validity of the extraction protocols in terms of solid phase dissolution. The two chemical fractionation methods are compared in terms of performance of implementation and results, to provide managers with valuable information on the most convenient method in view of an optimal treatment of basin sediments.

2. Materials and methods

2.1 Field sites and sediment sampling

The sediments were sampled in three stormwater infiltration basins located in Nantes and Lens (respectively in the West and North of France). The first site selected for this study, i.e. Boisbonne basin, is located in the East of Nantes. The drained runoff waters come from a

16,000 m² contribution area of the A11 highway. The average daily flow is about 27,000 vehicles. The Boisbonne basin was built in 1992 and had never been dredged since this date (figure 1(a)). The second basin, named Cheviré basin, is located South West of Nantes. It receives runoff waters from a 19,000 m² contribution area of the southern part of the Cheviré bridge which is a section of the Nantes ring-road (figure 1(b)). Opened in 1991, the Cheviré bridge now carries an average daily flow of 90,000 vehicles. The third basin (G08), located in the industrial area of Lens, drains runoff waters from a 14,000 m² contribution area of the A21 highway and carries an average daily flow of 80,000 vehicles (figure 1(c)). Since its opening in 1971, the basin had never been dredged. Specific zones are identified within each basin, based on both the uneven flow of water inside the basins and the development of vegetation (table 1). The entire surface of Cheviré and G08 basins is affected by infiltration of runoff waters, whereas the Boisbonne basin has a zone (BB1) remaining subaqueous (figure 1(a)). All infiltration zones are prone to changing redox conditions.

The samplings were performed in June 2009 for Boisbonne and Cheviré basins and in December 2009 for G08 basin. The sampled sediment layer can be distinguished from the underground soil by its black colour, its texture and its structure. The thickness of this layer ranges from a few centimeters to 30 cm, depending on the zones. The sediment sampling was conducted on the whole thickness and on each zone of the three basins (3 zones for Boisbonne (figure 1(a)), 4 zones for Cheviré (figure 1(b)) and 4 zones for G08 basin (figure 1(c)) according to the frequency and speed of flooding in the different areas (table 1). For each zone, a representative sample was composed with an homogeneous mixture of 6 to 13 shots (depending on the size of each area) within a grid system distribution [12]. Only one representative sample of each zone was then analyzed.

2.2 *Chemical and mineralogical sample characterization*

The pH value was measured in sediment/water suspensions (solid/liquid: 1/5 (V/V); NF ISO 10390 [13]) and using a TIM 900 (Radiometer Analytical TitraLab®) titration system. Total organic matter (TOM) content was determined by calcination at 550°C during 2 hours.

Total element contents, especially trace metal concentrations (Cd, Cr, Cu, Ni, Pb and Zn) were determined on samples sieved to 2 mm and dried at 40°C. The analyses were performed after mineralization of the samples by use of a mixture of HF and HClO₄ acids (NF X 31-147 [14]). Analyses on a certified reference material BCR-320 (river sediment) were carried out to assess the quality of the analytical data. Determination of chemical element contents was performed by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES; Varian 720-ES). The quantification limits for Cd, Cr, Cu, Ni, Pb and Zn are respectively 0.5, 5, 2, 10, 10 and 2 µg.L⁻¹. In case of concentration under the limit of quantification, the sample was analyzed by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS; Varian 820-MS). The ICP-MS limit of quantification for trace elements is ranging from 0.02 µg.L⁻¹ to 0.3 µg.L⁻¹ depending on the element.

A Brüker "D8 Advance" powder diffractometer operating in Bragg-Brentano geometry ($\theta/2\theta$) was used to identify the major crystalline phases by X-ray diffraction (XRD). This diffractometer is equipped with a copper anode and a germanium monochromator (Cu_{K α 1} λ = 1.540598 Å) with a Vantec position sensitive detector. Diffractometer settings were 40 kV, 40 mA, 3.500 - 67.992° 2 θ , step size 0.017° 2 θ and 1 s counting per step. The phase identification was performed using EVA software in conjunction with the Powder Diffraction File (PDF) database. The sediment samples were analysed by scanning electron microscopy (SEM) performed with a Hitachi S 570. Two observation modes are available: the imaging mode collecting low-energy secondary electrons to observe the surface topography of particles (LaB₆ tip, 30 kV maximum), and Energy Dispersive X-ray spectroscopy (EDX

spectroscopy) analysis to get qualitative elemental composition between 1 and 10 keV (limit of quantification 1000 ppm).

2.3 Extraction procedures

The sequential and kinetic extraction procedures were carried out on each zone of the three basins, Boisbonne (BB1 to BB3), Cheviré (CH1 to CH4) and G08 (G08z1 to G08z4). In order to verify which minerals dissolved during the extractions, XRD patterns were obtained prior to and after each extraction step of the sequential extraction and after 72 h of contact for kinetic extraction [15;16]. The same samples were also characterized by SEM-observations. Metal analyses were performed using an ICP-OES and/or ICP-MS as described above.

2.3.1 Sequential extraction

Despite criticisms, sequential extractions have been frequently used for trace metal location in contaminated soils and in river and marine sediments [8]. The most widely applied method is derived from that proposed by Tessier et al. (1979) [17]. The European Community Bureau of Reference (BCR) has proposed an optimized three-step procedure, including an application for sediment with the production of Certified Reference Material [18;19]. According to this procedure, the first extractable fraction, the exchangeable fraction, is related to clay, carbonates and amorphous phases, the second one is the reducible fraction related to metal (hydr)oxides and the third one is the oxidisable fraction related to organic matter. A fourth step was added consisting of mineralization of the final residue by use of a mixture of concentrated HF/HClO₄. This step is supposed to extract the residual fraction. The different steps are summarized in Table 2. The extraction procedure was conducted on 2g dry sample (uncrushed and sieved to 2 mm). The liquid-solid separation was performed by centrifugation and filtration of the supernatant on 0.45µm Millipore filter. Metal analysis was performed by ICP-OES and/or ICP-MS as described above (section 2.2).

Blank tests were introduced in each series. Cd, Cr, Cu, Ni, and Pb concentrations of blank samples were always below ICP-OES and ICP-MS quantification limits, Zn concentration is lower than 0.01 mg.L^{-1} which is negligible by comparison to Zn concentration in the extracted samples (over 10 mg.L^{-1}). The quality of the analyses was assessed by analyzing a reference sediment BCR-527 (lake sediment), using the same procedure. A statistical test (two-sided t -test), used for significant differences from the reference content, confirmed that the experimental values are not significantly different from the certified values ($P>0.05$), except for copper, which is over estimated in step 1.

2.3.2 *Kinetic extraction*

Kinetic extractions are also a widely used method to investigate kinetic aspects that characterize the stability of the various trace metal–soil/sediment constituent association [20]. For a given agent, the kinetic extraction approach generates two kinds of data: (i) the proportion of metal extracted with respect to the total metal content of sediment sample; (ii) the kinetic behavior of metals. It has been suggested that kinetic extractions can be modeled by two different pools. Although chemical extractants used for experiments do not perfectly mimic natural conditions, the first pool of readily extracted metals, called “labile” [21], and the second one of more slowly extracted metals, called “non labile”, might be reasonably attributed to potentially “mobile” and/or “bioavailable” metal pools [22]. In addition, the total non-extractable fraction is defined as the difference between the total amount of metal in sediment and the two above mentioned pools [23]. Several reagents are used for the kinetic extractions but EthyleneDiamineTetraacetic Acid (EDTA), a well known strong chelating agent, has been often used in soil studies for estimating the total extractable metal pool. As EDTA is a non specific reagent, it was reported to remove organically bound metals as well as those in oxides or secondary clay minerals [29]. This procedure was applied on various

soils and river sediments to mimic mobility aspects of heavy metals but never on stormwater infiltration pond sediments [11;21;23;24].

Kinetic extractions by EDTA were used on sediment samples to study :i) the maximal potential metal extraction capacity after 72 h; and ii) the extraction rates of metals released as a function of time (between 0 and 72 h). The EDTA kinetic extraction was conducted on dry sample of each zone for the three basins (11 samples). For each zone, a series of 12 x 1 g samples was mixed with 50 mL of pH 7 solution of EDTA (0.1 M) using a rotary stirrer for 12 mixing periods (5, 15 and 30 min; 1, 2, 4, 8, 16, 24, 36, 48 and 72 h). The liquid-solid separation was performed by centrifugation and filtration of the supernatant on a 0.45 μ m Millipore filter. A series of blank tests was added to the samples. The analysis of metals was performed by ICP spectrometry as described above (section 2.2). As for sequential extractions, the blank concentrations for trace metals are negligible.

The amount of each metal extracted for the mixing t time was at first calculated (example in figure 2(a)). Then the amount of metal extracted per solid weight unit (M) and the average removal rate per time unit ($A_M(t)$) are calculated. The evolution of $A_M(t)$ can generally be described by two distinct linear segments representing two distinct pools and reacting with two different kinetics (figure 2(b)). Three compartments associated with the two reaction rates were defined: (i) the labile compartment Q_L , associated with a kinetic constant k_L , (ii) the non-labile compartment Q_{NL} , associated with a kinetic constant k_{NL} and (iii) the non-extractable compartment Q_{NE} , obtained by subtracting Q_L and Q_{NL} of total amount of metal ($Q_L + Q_{NL} + Q_{NE} = \text{total amount}$). Labanowski et al. (2008) [23] described in details the general procedure of modeling and assessment of these three compartments.

3. Results and discussion

3.1 *Mineralogical and chemical characteristics of the bulk sediments*

SEM observations indicate that the three sediments are mainly composed of single particles (figure 3(a)) and aggregates (figure 3(b)). The single particles are mainly primary minerals identified by XRD: quartz, albite (Na feldspar), microcline (K feldspar) and mica. Clay mineral (peak at 14 Å and 7 Å) occurs as a minor phase in Chevire and G08 sediments. The XRD analysis revealed the presence of an additional carbonate phase (calcite) in G08 sediments (figure 4 – untreated sample). The presence of these well crystallised mineral phases is related to the nature of the soil beneath the basins and to the local geological context, which controls the nature of the mineral particles in runoff waters. Sand constitutes the bottom of the Nantes basins, the parent rock being micaschists. The G08 basin is located in limestone formations. The aggregates have a size ranging from 10 to 300 µm and are composed of both the primary minerals and an organic binding phase. Such aggregates were previously observed as dominant components in the sediment of an infiltration pond near Lyon (France) [25].

The main chemical characteristics of the bulk samples are presented in Table 3. The characteristics (pH, TOM, chemical content) of the Chevire sediments are similar to those reported in previous studies [26-28].

The higher concentrations of calcium (and probably magnesium) in G08 sediment by comparison to Chevire and Boisbonne sediments are related to the presence of calcite as mineral phase. This carbonated phase is also responsible for the high pH value of G08 samples. In spite of similar organic matter (OM) contents, pH values for Chevire and Boisbonne sediments are quite different. This result could be explained by the nature of the organic matter present in the sediments. As described in previous studies [9;25,29], the organic matter of stormwater sediments is attributed to both natural and anthropogenic contributions, related to the development of vegetation and to the nature of OM in runoff waters. Anthropogenic organic matter may originate from oil and fuels as well as from

vehicle and infrastructure corrosion (tire and road fragments) [30]. Neutral pH values are reported in the literature [6]. Otherwise, Boisbonne pH values are in the range of those of organic natural soil (around 5). This is relevant with the lower contamination of Boisbonne sediment, that should be related to a low amount of anthropogenic OM received. Unlike the homogeneity in terms of mineralogical composition, the total organic matter (TOM %) contents are different from one area to another for Cheviré and Boisbonne basins. For G08, the distribution is fairly similar for the four areas. The highest TOM content is found within BB1, CH4 and G08-z3 zones located near the overflow outlet (figure 1). This observation is consistent with the results of previous study Cannavo et al. (2010) [28]. This result could be explained by the heterogeneity of the sedimentation process within the basins.

Trace metal contents are compared to the Dutch intervention thresholds [31], used as reference. The thresholds are applied to a standard soil containing 25% clay ($< 2\mu\text{m}$) and 10% organic matter. So for each type of soil (different clay and/or organic matter content) thresholds should be adjusted using two correction formulas [32]. According to these corrected thresholds, G08 basin is the most contaminated basin. It is polluted with Cd and Cr, whereas Cu, Pb and Zn concentrations are above the intervention value. Cheviré samples are highly loaded with Cu, Pb and Zn, and concentrations are above the intervention thresholds for Cu and Zn. Boisbonne samples are the less polluted with trace metals. This basin is polluted with Cd (only BB1), Cu, Ni and Zn but concentrations never exceed the intervention thresholds. The differences in trace metal content can be explained by the age of the basins (G08 is the older), the traffic, the atmospheric contribution, the mineralogy and the pH values, knowing that a low pH favors trace metal leaching. No trace metal (Zn or Pb) was detected by EDX-spectroscopy within samples containing Pb and Zn concentrations above 1000 mg.kg^{-1} . This result may be attributed to the heterogeneity of trace metal distribution within the sample and to the high aggregation state.

3.2 Sequential extraction

Results of trace metal fractionation obtained by sequential extractions for the three basins are presented in figure 5. Results are expressed in percent of the total content, in the four operationally defined fractions. For a given element, the mass balance was calculated by dividing the sum of concentrations from the four extraction steps by the total concentration measured on bulk sediment. The balances were in the range 78 to 100% (figure 5). The recovery is over 82% for 83% of the trials. The lower recovery rates could be related to the aqueous washing between two extraction steps and to losses of matter due to spattering reaction of samples when adding H₂O₂ (step 3), leading to an under-estimate of trace metal amounts bound to organic matter or very stable mineral phases.

Trace metal distribution. The results show that inside a same basin, the partitioning of trace metals between the different fractions is quite homogeneous with a standard deviation of less than 20% in 70% of the cases. In order to synthesise the results thereafter, only data from one representative area are presented for each basin: BB2 for Boisbonne, CH4 for Chevire and G08z2 for G08 (figure 5).

The results of sequential extractions clearly suggest that the fractionation of trace metals in Chevire sediment was always more similar to those of G08 sediment than Boisbonne sediment. Fractionation of elements such as Cd, Cr and Ni was close for the three basins: exchangeable Cd accounted for 55 to 66% and large amounts of Cr and Ni (50-75%) remained in the residual fraction, except for Ni in Boisbonne sediment which is equally distributed among exchangeable and residual fractions. Cu and Pb of Chevire and G08 basins are predominantly bound to metallic hydr(oxides) and organic matter, whereas most Zn was released by step 1 and 2 (exchangeable Zn, weakly complexed Zn, Zn bound to hydr(oxides)). The results for the Boisbonne sediment show that substantial amounts of Cu, Pb and Zn (30 to 40%) remained also in residual fractions. The differences between Chevire/G08 and Boisbonne sediments are attributed to the variation of trace metals speciation in sediments

due to the nature of organic matter, ratio between geochemical background and anthropogenic contamination and low pH of the sediment.

The results of sequential extractions for the Cheviré sediment are consistent with previous studies [9,33], except for lead which was more released from the oxidisable fraction of the sediment sampled in 2001 (40% against 27% (this study)). Before 2000 in France, the main sources of lead in road environment were leaded gasoline, brake linings and deicing salts [34]. Since the removal of lead from fuels, the lead species contained in automobile exhausts disappeared in runoff waters. It was shown that Pb (originally labile in gas combustion) was rapidly transformed into particulate and non-labile forms [30]. One can suggest that these specific forms of lead, which don't exist anymore, were released from oxidisable fraction (step 3 of sequential extraction procedure) of sediment sampled a few years around 2000.

Cr, Cu, Ni, Pb and Zn distribution was studied by sequential extraction among lake sediments [15], those materials being characterized by the same mineralogical composition than the sediments of the basins (except for calcite). The distribution of Cu, Pb and Zn among the operationally-defined fractions is very similar to those observed for Cheviré, G08 and especially Boisbonne. This underlines again the more natural character of the organic matter of the latter basin. On the other hand, the comparison of our results with those of sediments contaminated by Pb-Zn mining is much less easy [16]. In this later study, Pb was predominantly bound to (hydr)oxides (reducible fraction) but remained also in the residual fractions. Zn is partly in the exchangeable fraction but principally distributed among the oxidisable and residual fractions. The speciation of heavy metals acquired during their emission has therefore a very strong impact on their later mobility.

XRD and SEM study. The XRD analyses and SEM observations of samples after each step of sequential extractions were very similar for the 3 basins. A representative diffractogram of G08z2 sample illustrates the general XRD results (figure 4). The XRD method used in this

study does not allow quantitative analyses, thus it is only possible to conclude about the presence or not of the crystallised minerals. The main mineral phases i.e., quartz, feldspar, mica and clay were recovered in the samples obtained after each step of the sequential extractions. This indicates that there is no or non distinguishable (by this method) dissolution of these primary minerals which could compromise the interpretation of the results on metals fractionation. Calcite (peak at 3Å) is completely dissolved within step 1 of the sequential extractions. Therefore trace metals bound to this solid phase are entirely solubilised. The first three residues of sequential extraction were observed by SEM. As for bulk samples, no trace metal was analysed with EDX-spectroscopy. After the first and the second steps of the sequential extraction, single mineral particles appear to be damaged. This degradation could result from the effect of the reagent or from the frictional effects during stirring. By contrast, the aggregates have the same morphology (size, shape) and composition as before the extraction procedure (figure 3(b)). However, after the third step, the aggregates are partly destroyed or broken, leading to finer aggregates mostly sized from 10 to 50 µm. This observation is consistent with the work on stormwater infiltration sediment from Lyon [25], which shows that H₂O₂ damages the larger aggregates of an infiltration pond sediment with a resulting size decrease (%D50 from 55 to 10 µm). This means that the removal of the organic matter partly destroys the aggregates and that OM plays a significant role as binding phase in aggregates. Furthermore, small aggregates are still observed after each step. It means that these aggregates play a significant role in the retention of trace metals located in the oxidisable (related to organic matter) and residual fractions. Indeed, Cu and Pb were highly released during step 3, as the aggregates were partly destroyed by oxidation of the organic matter. In the residual fraction, trace metals such as Cr and Ni, which are not solubilised by the reagents of the first three steps, are strongly stabilized in aggregates. Due to the disaggregation of some of the aggregates during steps 3 and 4, one could have expected to

observe higher metal concentrations on solid phases (at least in the case of Zn). However, no trace metal was analysed by EDX-spectroscopy, confirming that the trace metals are highly concentrated on a few particles, which location and observation are difficult due to a heterogeneous distribution in the sediments.

3.3 *Kinetic extraction*

Results of trace metal fractionation obtained by kinetic extractions for the three basins are presented in figure 5. Results are expressed in percent of the total content, in the three compartments (Q_L , Q_{NL} and Q_{NE}) of the kinetic extractions. The sum of $Q_L + Q_{NL} + Q_{NE}$ is normally 100%. In figure 5, some recoveries are over 100%, particularly for Cu, the main explanation is that Q_L compartment is overestimated by the method.

Trace metal distribution. As for sequential extraction procedure, inside a same basin, the partitioning of trace metals between the different compartments is homogeneous (standard deviation less than 30% in 86% of the cases, excluding Cd and Q_{NE} compartment). As for sequential extraction, only data from one representative area are presented for each basin (BB2, CH4 and G08z2) (figure 5).

The distribution of trace metals between labile, non labile and non extractable compartments could be summarized as follows: Cd, Cu, Pb and Zn (only for Boisbonne basin) are highly labile; Cr and Ni (for Chevire and G08 basins) are clearly non extractable; and Zn from Chevire and G08 basins is fairly distributed between the three compartments. Kinetic extractions have never been achieved on sediments from runoff water infiltration basins. The comparison of our results with weakly contaminated river sediments [11] does not show the same behavior of Cd, Cu, Pb and Zn between Q_L , Q_{NL} and Q_{NE} compartments. On the other hand, Cd, Pb and Zn distributions between the three compartments in a contaminated soil mimic our results [23].

XRD and SEM study. As for sequential extractions, the XRD analyses and SEM observations of samples after kinetic extractions were very similar for the 3 basins. The XRD pattern of the residue after 72 h of contact with EDTA for zone 2 from G08 basin (G08z2) is presented in figure 4. The main mineral phases (quartz, feldspar, mica and clay) were detected indicating that there is no or few dissolution of minerals. As for the sequential extraction residue, calcite (peak at 3Å) is almost completely dissolved thereby solubilising trace metals bound to this phase. No trace metal was detected by EDX-spectroscopy within the residues after 72h of contact with EDTA. The SEM observations highlight that the residues are similar to the untreated samples, with a slight damage to the minerals (single particles). We can deduce from these latest observations that the damage on the minerals, observed for the residues after sequential extraction steps, was mainly due to the reagent effects and not to stirring effects. Moreover, as for sequential extraction steps, aggregates (10 to 300 µm) are still observed after 72 h of contact with EDTA. This result confirmed the important role of aggregates belonging to the non-extractable compartment, in the retention of trace metals. Trace metals in the non-extractable compartment were not solubilised by EDTA indicating a strong stabilization in aggregates.

3.4 Comparison of trace metal fractionation

The comparison of the two extraction procedures aimed at highlighting the complementarity of the two methods in describing trace metal fractionation. Indeed, despite the shortcomings of the sequential extraction method including incomplete dissolution of target phases, incomplete removal of dissolved species due to readsorption or reprecipitation, (according to trace metals adsorption/desorption properties), the comparison of both the fractionations allows to draw some trends.

The comparison of the two extraction methods highlights that:

346 - Cd from exchangeable and reducible fractions appears to be labile, whereas Cd contained in
347 the residual and oxidisable fractions (for G08) is non labile. The fractionation of chromium is
348 homogenous throughout all the sediments: residual and oxidisable fractions are the bearing-
349 phases of the non extractable chromium.

350 - Regarding copper, results of sequential and kinetic extractions are hardly compared. The
351 high complexation capacity of Cu with EDTA could be responsible for its strong lability and
352 explain the discrepancy between both extractions.

353 - a large part of nickel is labile (52%) and the remaining is largely non extractable (57%).
354 However, the comparison between sequential and kinetic extractions leads to the same
355 comment for the three basins, i.e., nickel from the exchangeable fraction is labile, the
356 reducible fraction is non labile and Ni from the oxidisable and residual fractions is non
357 extractable.

358 - Lead from the exchangeable and reducible fractions is labile, Pb from the oxidisable fraction
359 is non labile and Pb from the residual fraction is non extractable.

360 - and that Zn from the exchangeable fraction is labile, that from the reducible fraction is non
361 labile and that from the oxidisable and residual fractions is non extractable.

362 Thus it can be drawn that: i) trace metals from the exchangeable fractions are always labile,
363 whereas those from the residual fraction are non extractable; ii) the reducible fraction
364 corresponds to labile or non labile compartments; iii) and the oxidisable or organic matter
365 fraction seems to correspond to the non labile or non extractable compartments. In terms of
366 bounding strength between trace metals and solid surfaces, trace metals are strongly adsorbed
367 on organic phases (oxidisable fraction) or tightly included in the residual fraction as revealed
368 by the level of extraction from the non labile or the non extractable compartments. Cd, Cr, Cu
369 and Pb are weakly adsorbed on metal oxides (reducible fraction), whereas Ni and Zn are
370 strongly adsorbed on metal oxides. Complexation data from the literature indicate the

following order of affinity between EDTA and metallic ions: Cu>Ni>Pb>Zn. Trace metals, such as Cu, Pb and Zn are in fact quantified in the labile compartment but it is not the case for Ni. As Ni was largely non-extractible, one can outline the main role of the speciation (chemical form) of trace metals in runoff waters on their mobility capacity within the sediment.

3.5 Findings summary

Aggregation and extraction efficiency. Decidedly, the most unexpected result of this study is the documentation of the evolution of aggregate state within the extraction steps and their role in the retention of trace metals. Previous studies have suggested that sequential extraction procedures are not perfectly selective with respect to mineral dissolution, and without quantitative XRD, the minerals that dissolve with each successive extraction are operationally defined [15]. In this study, we showed that not only isolated mineral phases but also aggregates (depending on their disintegration state) contribute to trace metal mobilization. SEM observations gave essential information that could not be obtained by XRD. However, it would be necessary to use complementary techniques to assess the dissolution of amorphous or poorly crystallised metallic oxides and hydroxides.

Moreover, this study underlines that a part of trace metals is really stabilized in aggregates (small aggregates (10-50 μm)). Therefore, if the partitioning of the stable aggregates from the instable and single particles could be achieved, it would be possible to reuse the sediments after the sole treatment of the non aggregated fraction and thus reduce the treatment costs.

Is kinetic extraction a convenient method to quantify heavy metal potential mobility?

One of the objectives of this study was to assess the relevance of a simple method such as EDTA extraction to optimize sediment treatment. The results showed that metallic pollutants are distributed among two categories: i) copper, cadmium and lead, which have a low EDTA non extractable fraction; ii) chromium, nickel and zinc present in oxidizable and residual

fractions which are non EDTA extractable. For Cu and Pb, the use of EDTA extraction appears to be relevant. It will give a rough under estimate of stable amounts of metals. For Cd, it is difficult to conclude from the results of this study. For Cr, Ni and Zn, the use of EDTA extraction over estimates the very stable metal fraction, as the oxidizable fraction was included. As the degradation of OM, a major constituent of sediment aggregates which can be strongly modified by drying, remoisting or biological degradation is likely to release trace metals, the EDTA extraction could not be considered as a convenient method to evaluate the stable fraction of Cr, Ni and Zn.

It would be interesting, in the case of stormwater sediments, to compare these kinetic extractions results with leaching tests representative of natural conditions. This will assess the relevance of: i) the kinetic extractions method and ii) the extractant used. Such comparisons were conducted on contaminated soils [23]. The findings of the study indicate that EDTA extractions provide an indication for the maximum potential metal extractability, helpful for the prediction of long-term risks.

Can these conclusions be applied to all stormwater sediments? This study shows that metals have a rather similar behaviour from one basin to the other, indicating that the chemical extraction used seems to overcome physicochemical conditions such as pH or redox conditions (for BB1 subaqueous area). However, in natural conditions, pH and redox conditions are recognized to highly influence metal speciation and stability. It raises the question of trace metal sources. For these three road basins, the sources are quite similar.

How can these conclusions guide manager's decisions? The comparison between sequential and kinetic extractions has provided information on trace metals fractionation and stability within stormwater sediments. The coupling of these procedures with XRD analyses and SEM observations has highlighted that organic matter plays a significant role as binding phase in aggregates and underlined the influence of aggregates in the retention of trace metals.

As this approach is new for stormwater sediments, a validation of these results is necessary. Kinetic extraction results should be confronted to leaching tests representative of natural conditions to predict long-term risks and trace metal fractionation could be compared to the distribution of these same trace metals in fractions obtained by physical fractionation of sediment solid phases, as density fractionation. After validation, these methods will allow to access quickly and easily to information on trace metal distribution and their stability within stormwater sediments. The localization of the metals will permit to treat only the fractions containing the labile trace metals. Information on trace metals stability will allow the reuse of the whole or the non-treated part of the sediment. In this case, additional physicochemical characteristics should be known i) pH and redox conditions and ii) TOM contents (to evaluate aggregation state).

4. Conclusion

In this paper we used several indirect and direct techniques to characterize the trace metal fractionation in sediments from runoff water infiltration basins. Our objective was to access to trace metal potential mobility within physical phases as a mean to improve the management of stormwater sediments.

The comparison of sequential and kinetic extractions shows that trace metals from the exchangeable fraction are always labile, whereas those from the residual fraction are non extractable. Trace metals associated to the reducible fraction are labile or non labile, whereas those bound to organic matter (oxidisable fraction) are non labile or non extractable. The coupling of these procedures with XRD analyses and SEM observations has allowed: i) to ensure the slight or non-dissolution of mineral phases (except calcite); ii) to highlight that organic matter plays a significant role as binding phase in aggregates and iii) to underline the

445 influence of aggregates in the retention of trace metals, especially a remaining fraction of very
446 stable small aggregates was observed.

447 One single method is not sufficient to explain the fractionation and the mobility of trace
448 metals in the different fractions and this study highlighted the complementarity of the two
449 extraction methods for a better understanding of trace metal distribution among solid phases.
450 This methodology could serve as a tool for a better assessment of trace metal behaviour for
451 the management of sediment from stormwater infiltration basins. Several methods have been
452 proposed for the treatment of stormwater sediments; among the recent ones sieving coupled
453 with attrition has proved quite efficient. The decision to treat sediment is based on bulk
454 concentration determination; however, a better knowledge of metal mobility, as proposed in
455 this study, might be useful. In case the metals of concern appear not to be mobile (e.g.
456 localized in the residual fraction), treatment could be avoided, hence saving money.

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FIGURES CAPTIONS

Figure 1 Schemes of a) Boisbonne, b) Cheviré and c) G08 basins

Figure 2 Evolution in time of Ni: a) extracted amount, b) removal rate for G08z2 sample

Figure 3 SEM observations: Cheviré zone 4 (CH 4): a) mica particle (x 800) ;b) an aggregate (x 1100) - G08 zone 2 (G08z2)

Figure 4 XRD analysis of a G08 sample (zone 2) after the different sequential extraction steps and 72h of contact with EDTA. C= clay, M= mica, F= feldspar, Q= quartz and Cal. = calcite.

Figure 5 Distribution of trace metals between sequential extraction fractions (left) and between kinetic extractions compartments (right) for Boisbonne (B-SE and B-KE), Cheviré (C-SE and C-KE) and G08 (G-SE and G-KE) basins: a) Cd, b) Cr, c) Cu , d) Ni, e) Pb and f) Zn

Table 1 Characteristics of the basin zones

Basin	Zone	Flow	Vegetation
Boisbonne	BB1	Perennially subaqueous	Floating plants
	BB2	Permanent water supply with variable flow (drainage and surface runoff)	Herbaceous
	BB3	Intermittent, related to rain events (only road runoff)	Herbaceous and reeds
Cheviré	CH1	Turbulence zone	Only brambles
	CH2	Major flood zone	Herbaceous
	CH3	Raised zone	Herbaceous and shrubs
	CH4	Slow sedimentation zone	Herbaceous and rush
G08	Z1 to Z4	Same flow conditions across the whole surface	Herbaceous

Table 2 Sequential extraction procedure

Step	Reagent	Operating conditions	Fraction	Extracted phase
1	80 mL of 0.11 M acetic acid	Stirred 16h at ambient temperature	Exchangeable	Acid-soluble and exchar
2	80 mL of 0.1 M hydroxylamine hydrochloride (pH 2)	Stirred 16h at ambient temperature	Reducible	Fe and Mn oxides
3	2 x 20 ml of 8.8 M H ₂ O ₂ 100 mL of 1M ammonium acetate (pH 2)	1h at ambient temperature and 1h at 85°C Stirred 16h at ambient temperature	Oxidisable	Organic matter
4	Concentrated HF/HClO ₄	After calcination at 450°C	Residual	Residual

Table 3 Main physicochemical characteristics of the three sediments

		TOM*	pH	Ca	Mg	Trace metals contents (mg.kg ⁻¹)					
		(%)	(in water)	(g.kg ⁻¹)	(g.kg ⁻¹)	Cd	Cr	Cu	Ni	Pb	Zn
Boisbonne											
	BB1	17	5.2	3.8	5.3	1.2	54	59	75	41	480
	BB2	9	4.4	2.2	3.3	0.4	43	27	34	32	132
	BB3	16	4.8	3.5	4.7	0.4	54	30	39	31	139
Cheviré											
	CH1	7	7.5	18.0	6.0	0.5	48	190	20	70	784
	CH2	11	6.9	10.0	7.1	0.8	74	335	30	152	1274
	CH3	12	6.7	9.7	7.8	0.9	79	320	32	250	1714
	CH4	16	6.3	10.0	8.9	1.2	92	366	37	368	1863
G08											
	G08_z1	17	8.0	42.5	9.4	9.3	120	498	56	1130	2574
	G08_z2	17	8.2	48.7	9.5	9.6	111	489	54	1064	2587
	G08_z3	18	7.8	52.9	9.3	9.1	129	514	53	1099	2508
	G08_z4	16	7.8	46.0	9.3	9.2	112	457	54	1235	2595
Dutch standard (reference)											
Polluted soil ⁽¹⁾						0.8	100	36	35	85	140
Intervention threshold ⁽²⁾						12	380	190	210	530	720

* Total organic matter; ⁽¹⁾ Value at which a soil is considered contaminated; ⁽²⁾ Value at which intervention is necessary [35]